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Microbeam analysis — Quantitative analysis using energy-dispersive spectrometry (EDS)

Analyse par microfaisceaux — Analyse élémentaire quantitative par spectrométrie à sélection d'énergie (EDS)

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 22309 was prepared by Technical Committee ISO/TC 202, *Microbeam analysis*.

Introduction

X-rays generated when a high-energy electron beam interacts with a specimen have energies (wavelengths) which are characteristic of the chemical elements (atom types) present in the specimen. The intensity of these X-rays from each element is related to the concentration of that element in the specimen. If these intensities are measured, compared with those from a suitable reference material or set of reference materials, and corrected in an appropriate manner, the concentration of each element can be determined. “Standardless” procedures also provide quantitative information, but involve a comparison with previously measured reference intensities that are stored within the software package or are calculated theoretically; such procedures may, depending on any assumptions made, be inherently less accurate than the method employing reference materials (see References [1] to [8] in the Bibliography). There are two common methods of detecting the characteristic X-rays that are produced, one which relies on wavelength dispersive spectrometry (WDS) and the other which uses energy-dispersive spectrometry (EDS). This International Standard relates to the latter, energy-dispersive spectrometry.

Using EDS, the quantitative analysis of light elements (i.e. atomic number $Z < 11$, below Na) is more complex and some of the problems are discussed in this International Standard.

Microbeam analysis — Quantitative analysis using energy-dispersive spectrometry (EDS)

1 Scope

This International Standard gives guidance on the quantitative analysis at specific points or areas of a specimen using energy-dispersive spectrometry (EDS) fitted to a scanning electron microscope (SEM) or electron probe microanalyser (EPMA); any expression of amount, i.e. in terms of percent (mass fraction), as large/small or major/minor amounts is deemed to be quantitative. The correct identification of all elements present in the specimen is a necessary part of quantitative analysis and is therefore considered in this International Standard. This International Standard provides guidance on the various approaches and is applicable to routine quantitative analysis of mass fractions down to 1 %, utilising either reference materials or "standardless" procedures. It can be used with confidence for elements with atomic number $Z > 10$.

Guidance on the analysis of light elements with $Z < 11$ is also given.

NOTE With care, mass fractions as low as 0,1 % are measurable when there is no peak overlap and the relevant characteristic line is strongly excited. This International Standard applies principally to quantitative analyses on a flat polished specimen surface. The basic procedures are also applicable to the analysis of specimens that do not have a polished surface but additional uncertainty components will be introduced.

There is no accepted method for accurate quantitative EDS analysis of light elements. However, several EDS methods do exist. These are the following.

a) Measuring peak areas and comparing intensities in the same way as for heavier elements. For the reasons explained in Annex D, the uncertainty and inaccuracy associated with the results for light elements will be greater than for the heavier elements.

b) Where the light element is known to be combined stoichiometrically with heavier elements ($Z > 10$) in the specimen, its concentration can be determined by summing the appropriate proportions of concentrations of the other elements. This is often used for the analysis of oxygen in silicate mineral specimens.

c) Calculation of concentration by difference where the light element percentage is 100 % minus the percentage sum of the analysed elements. This method is only possible with good beam-current stability and a separate measurement of at least one reference specimen and it requires very accurate analysis of the other elements in the specimen.

Annex D summarises the problems of light element analysis, additional to those that exist for quantitative analysis of the heavier elements. If both EDS and wavelength spectrometry (WDS) are available, then WDS can be used to overcome the problems of peak overlap that occur with EDS at low energies. However, many of the other issues are common to both techniques.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 14594, *Microbeam analysis — Electron probe microanalysis — Guidelines for the determination of experimental parameters for wavelength dispersive spectroscopy*

ISO 15632:2002, *Microbeam analysis — Instrumental specification for energy dispersive X-ray spectrometers with semiconductor detectors*

ISO 16700:2004, *Microbeam analysis — Scanning electron microscopy — Guidelines for calibrating image magnification*

ISO/IEC 17025:2005, *General requirements for the competence of testing and calibration laboratories*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
absorption correction
matrix correction arising from the loss of X-ray intensity from an element due to photoelectric absorption by all elements within the specimen while passing through it to the detector

3.2
accuracy
closeness of agreement between the “true” value and the measured value

3.3
accelerating voltage
potential difference applied between the filament and anode in order to accelerate the electrons emitted from the source

NOTE Accelerating voltage is expressed in kilovolts.

3.4
atomic number correction
matrix correction which modifies intensity from each element in the specimen and standards to take account of electron backscattering and stopping power, the magnitudes of which are influenced by all the elements in the analysed volume

3.5
beam current
electron current contained within the beam

NOTE Beam current is expressed in nanoamperes.

3.6
beam stability
extent to which beam current varies during the course of an analysis

NOTE Beam stability is expressed in percent per hour.

3.7
bremsstrahlung
background continuum of X-rays generated by the deceleration of electrons within the specimen

3.8
certified reference material
CRM
reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body

3.9
characteristic X-ray
photon of electromagnetic radiation created by the relaxation of an excited atomic state caused by inner shell ionisation following inelastic scattering of an energetic electron, or by absorption of an X-ray photon

3.10
dead time
the time that the system is unavailable to record a photon measurement because it is busy processing a previous event

NOTE This is frequently expressed as a percentage of the total time (see also live time).

3.11
energy-dispersive spectrometry
EDS
form of X-ray spectrometry in which the energy of individual photons are measured and used to build up a digital histogram representing the distribution of X-rays with energy

3.12
electron probe microanalysis
a technique of spatially resolved elemental analysis based on electron-excited X-ray spectrometry with a focused electron probe and an interaction/excitation volume with micrometre to sub-micrometre dimensions

3.13
escape peaks
peaks that occur as a result of loss of incident photon energy by fluorescence of the material of the detector

NOTE 1 These occur at an energy equal to that of the incident characteristic peak minus the energy of the X-ray line(s) emitted by the element(s) in the detector (1,734 keV for silicon).

NOTE 2 They cannot occur below the critical excitation potential of the detector material, e.g. Si K escape does not occur for energies below 1,838 keV.

3.14
fluorescence
photoelectric absorption of any X-ray radiation (characteristic or bremsstrahlung) by an atom which results in an excited atomic state which will de-excite with electron shell transitions and subsequent emission of an Auger electron or the characteristic X-ray of the absorbing atom

3.15
fluorescence correction
matrix correction which modifies the intensity from each element in the specimen and standards to take account of excess X-rays generated from element “A” due to the absorption of characteristic X-rays from element “B” whose energy exceeds the critical (ionisation) energy of “A”

3.16
full width at half maximum
FWHM
measure of the width of an X-ray peak in which the background is first removed to reveal the complete peak profile

NOTE FWHM is determined by measuring the width at half the maximum height.

3.17
incident beam energy
energy gained by the beam as a result of the potential applied between the filament and anode

3.18
k-ratio
net peak intensity (after background subtraction) for an element found in the specimen, divided by the intensity, recorded or calculated, of the corresponding peak in the spectra of a reference material

3.19
live time (s)
time the pulse measurement circuitry is available for the detection of X-ray photons

See also **dead time** (3.10).

NOTE 1 Live time is expressed in second (s).

NOTE 2 Live time = real time for analysis – dead time. Real time is the time that would be measured with a conventional clock. For an X-ray acquisition, the real time always exceeds the live time.

3.20
overvoltage ratio
ratio of the incident beam energy to the critical excitation energy for a particular shell and sub-shell (K, LI, LII, etc.) from which the characteristic X-ray is emitted

3.21
peak intensity
total number of X-rays (counts) under the profile of a characteristic X-ray peak after background subtraction

NOTE This is sometimes referred to as the peak integral.

3.22
peak profile
detailed shape of a characteristic peak which depends on the relative intensities and energies of the individual X-ray emissions that are unresolved by the energy-dispersive spectrometer

3.23
precision
closeness of agreement between the results obtained by applying the experimental procedure several times under prescribed conditions

3.24
quantitative EDS
procedure leading to the assignment of numerical values or expressions to represent the concentrations of elements measured within the analysis volume

3.25
reference material
RM
material or substance, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a method, or for assigning values to materials

NOTE A reference material is said to be homogeneous with respect to a specified property if the property value, as determined by tests on specimens of specified size, is found to lie within the specified uncertainty limits, the specimens being taken either from a single or different supply unit.

3.26
repeatability
closeness of agreement between results of successive measurements of the same quantity carried out by the same method, by the same observer, with the same measuring instruments, in the same laboratory, at quite short intervals of time

3.27
reproducibility
closeness of agreement between the result of measurements of the same quantity, where the individual measurements are made by different methods, with different measuring instruments, by different observers, in different laboratories, after intervals of time that are quite long compared with the duration of a single measurement, under different normal conditions of use of the instruments employed

3.28
resolution
⟨energy⟩ width of a peak measured by an energy-dispersive spectrometer and expressed as the peak width at half the maximum peak intensity

NOTE This is usually expressed as the value for Mn Kα (5,894 keV), although peaks from other suitable elements can be used.

3.29
resolution
⟨spatial⟩ spatial specificity of microanalysis

NOTE This is usually expressed in terms of a linear or volumetric measure of the region of the specimen that is sampled by the measured characteristic radiation.

3.30
standardless analysis
procedure for quantitative X-ray microanalysis in which the reference peak intensity in the k-value expression, (unknown/reference) is supplied from purely physical calculations or from stored data from a suite of reference materials; adjustments being made to match analysis conditions and augment incomplete reference data

3.31
sum peaks
artefact peaks that occur as a result of pulse co-incidence effects that occur within the pulse pair resolution of the pile-up inspection circuitry

NOTE These peaks appear at energies corresponding to the sum of those energies of the two photons that arrive simultaneously at the detector.

3.32
traceability
ability to trace the history, application or location of an entity by means of recorded identifications

3.33
uncertainty
that part of the expression of the result of a measurement that states the range of values within which the “true” value is estimated to lie for a stated probability

3.34
validation
confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled

3.35
X-ray absorption
attenuation of X-rays passing through matter, arising primarily from photoelectric absorption for X-ray energies and ranges appropriate to EPMA/EDS and SEM/EDS

4 Specimen preparation

4.1 Material for analysis shall be stable under variable pressure conditions and the electron beam. As-received specimens can be examined after simple cleaning, but surface inhomogeneity or topography will adversely affect the quality of the quantitative analysis.

4.2 For reliable quantitative analysis, the specimen shall present a flat, smooth surface normal to the electron beam. This requirement is usually met by the application of conventional metallographic or petrographic techniques. The area for analysis should be homogeneous over a region, typically a few micrometres in diameter, around the electron beam.

4.3 Solid specimens can be reduced to an appropriate size, making sure they undergo no transformation during the process. Prior to examination in the as-received condition, all surface debris should be removed using appropriate techniques, such as ultrasonic cleaning.

4.4 Specimens for sectioning should be embedded, where possible, in a conducting medium prior to metallographic or petrographic polishing using standard procedures. The medium shall be chosen with care, to avoid the possibility of the conducting component becoming smeared onto the specimen surface and mistaken for a component of the specimen by effectively altering the composition of the analysed volume.

NOTE 1 Polishing may be carried through to 1/4 µm grade diamond, provided this can be done without introducing relief effects. Complete removal of all scratches is not essential, provided areas for analysis are clean and relief-free.

Damage to the specimen during preparation should be avoided. Potential damage mechanisms include:

a) the effects of lubricant;

b) the removal of second phases (precipitates);

c) differential polishing of phases with different hardness, thus introducing relief to the surface;

d) strain introduced into the surface;

e) edge curvature.

With cross-sections, the specimen can be coated with a harder material to improve edge retention.

NOTE 2 See ASTM E3-01[9] for further guidance.

4.5 If optical examination is to be used for the location of areas for analysis, either prior to or while in the instrument, etching of the specimen may be necessary. The depth of etching should be kept to a minimum, being aware of the possibility of surface compositional changes or the development of undesirable topographic effects. Polishing away the etching may be needed after locating and marking the regions for analysis by reference to existing or added features, such as a scratch or hardness indent.

4.6 The specimen should have a good conductivity to avoid charge-up generated by electron beam irradiation. The specimen shall be connected to the instrument ground either through a conducting mount, or by a stripe of silver or carbon paint. Any exposed non-conducting mounting material may be covered with a conducting medium to avoid disturbance of the electron beam during analysis**.**

Carbon to a thickness of about 20 nm can be used as a conductive coating, although a metallic (e.g. aluminium) coating of lesser thickness may be used if carbon is unacceptable.

NOTE Coating with an element already present in the specimen changes the apparent composition of that element in the specimen, the magnitude of the effect being dependent on accelerating voltage and the thickness of the coating.

4.7 The prepared specimens shall be positioned in the instrument stage in such a way that, for the majority of work, the surface can be reliably held normal to the incident electron beam.

4.8 Reference materials should conform to ISO 14595[18] and shall be prepared in a similar way to the unknown specimens, e.g. polished, carbon coated, and positioned in the same orientation relative to the electron beam.

5 Preliminary precautions

5.1 With a suitable vacuum level and the electron beam on, preliminary checks to ensure beam stability (better than 1 % per hour variation in counts from a standard specimen) and stable detector performance should be made prior to commencing calibration and analysis procedures. Detector stability shall be monitored by measuring the detector resolution and energy calibration (see ISO 15632).

5.2 The energy scale of the detector system shall be checked or re-calibrated at regular intervals (e.g. daily) or whenever there is any doubt over the identity of spectral peaks. All calibration data and any departure from calibration shall be recorded.

5.3 The energy scale shall be checked using the line positions for two peaks, one of low energy (for example, Al Kα at 1,486 keV) and one of high energy (for example, Cu Kα at 8,040 keV). Suitable individual reference materials for this purpose are readily available. Alternatively, Kα peaks from two elements, such as Al and Cu, present in the same reference material can be collected into the same displayed spectrum..

NOTE 1 Where it is possible to monitor the zero of the energy scale, only a single spectral peak is needed for accurate calibration.

NOTE 2 Use of the line positions for two peaks from the same element, e.g. Cu Lα and Cu Kα, along with a simple fitting procedure may give reduced calibration accuracy because of the distortion of Cu Lα by Cu LI and Cu Lβ.

5.4 The full width at half maximum (FWHM) of a selected peak provides a measure of the detector resolution. It shall be measured at regular intervals following the procedure in ISO 15632, and shall be less than an acceptable limit (typically that corresponding to a deterioration of more than 10 % of the as-delivered resolution) for given settings of the pulse processing electronics. If these limits are exceeded, the system performance shall be investigated and revalidated if necessary. All such measurements shall be performed under identical conditions and be recorded.

NOTE For accurate quantitative analysis using peaks with an energy close to 1 keV, it is not advisable to use a detector for which the FWHM of Mn Kα exceeds 160 eV, and is preferably less than 135 eV.

5.5 The ratio of the intensities of the Cu Lα and Cu Kα peaks, or equivalent peaks from other elements, e.g. nickel, provides a measure of the detector efficiency and shall be determined at regular intervals and recorded. Where this decreases to an unacceptable level (typically not less than 2/3 of the as-delivered value), the system shall be revalidated by the manufacturer, particularly where standardless analysis is being carried out. The detector should conform to ISO 15632:2002, Annex B.

5.6 For standardless analysis, check the measured spectrum using the Duane-Hunt rule

NOTE Deviations of the high energy end of the bremsstrahlung background from the indicated high voltage means either charging of the specimen or a wrong high voltage indicated by the SEM. No quantitative analysis can be done in these cases.

6 Analysis procedure

6.1 The filament shall be saturated and sufficient time allowed for it to achieve adequate stability, for example better than 1 % over the anticipated duration of the analysis run. An accelerating voltage, of typically between 10 kV and 25 kV, shall be chosen to meet one or more of several criteria.

a) For efficient excitation and good peak intensity, an overvoltage of at least 1,8 is desirable. Thus, when utilising high energy lines of the order of 8 keV to 10 keV, a minimum accelerating voltage of 20 kV is recommended.

b) For analysis of low energy lines, e.g. 1 keV to 3 keV, it is desirable to minimise the magnitude of the absorption correction and possible errors arising from it, by operation at low beam voltages, e.g. 10 kV providing the excitation requirement a) is satisfied for the lines of interest.

NOTE At 10 kV, analysis of the elements from Z = 24 (Cr) to Z = 29 (Cu) will not be possible since the K lines are not adequately excited.

c) For accurate analysis, it is essential that the analysed volume shall be wholly contained within the feature under examination throughout the analysis period; such features may be surface layers, small inclusions, areas near to an interface, etc. Methods for the estimation of the influence of accelerating voltage on analysis area and analysis depth are given in ISO 14594, and may be used in the selection of an appropriate accelerating voltage.

6.2 The beam current shall be set to a value that is sufficiently large to enable an adequate count rate for the whole spectrum from the specimen, but not so large as to introduce electronic distortion or sum peaks into the spectra from pure elemental materials.

NOTE 1 Typical conditions for a Si-Li detector are input count rates of up to 10 000 counts/s and dead times less than 35 %. Total spectrum counts of approximately 250 000 are usually appropriate, although this depends on the concentration of the element of interest.

The count rate capabilities of the system should be checked by comparing a spectrum obtained at a low count rate with a spectrum obtained at the highest count rate to be used, to look for peak shift and pile-up distortion. A minimum of two checks on beam stability, using a Faraday cup on a known reference specimen, should be made prior to and following the analysis.

NOTE 2 In the SEM, however, the beam current available may be limited by the requirement to operate with a small spot size in the pursuit of good image resolution.

6.3 The specimen shall be correctly positioned under the electron beam:

a) Using the energy-dispersive spectrometer with an EPMA requires the specimen surface to be located in the focal plane of the optical microscope, and at the instrument-defined angle to the beam (usually 90 °). Positioning or accidental tilt errors may degrade the accuracy of the data reduction procedures that are applied.

b) In the SEM, the specimen height will be determined by the working distance that has been selected or is given by the manufacturers as appropriate for EDS. Specimen tilt shall be set to zero.

ISO 16700 provides details for setting the stage at 0° tilt.

6.4 Pulse-processing settings shall be chosen to give the optimum resolution possible, consistent with the desired count rate and dead-time settings suggested in 6.2.

6.5 Positions for analysis on the specimen shall be selected by reference to either the optical or scanning electron images. Homogeneity in the chosen regions shall be checked by carrying out preliminary line scans of the X-ray intensity from one or more of the major elements in the specimen, or point analyses at several random locations sufficiently far from phase boundaries.

Where an optical system is available for locating positions on the specimen, care should be taken that the centres of the optical and electron optical systems are coincident.

6.6 When reference materials are used, they shall be positioned, in relation to the electron beam, in exactly the same way as the specimen and coated with a similar thickness of conducting material. Spectra shall be collected from the specimen and all reference materials using the same analytical conditions, with at least one reference material being examined at the beginning and end of the run in order to confirm stability of the beam and other system parameters, e.g. baseline shift, gain drift, resolution and beam current.

6.7 A collection time shall be chosen which is sufficient to give the required total count within peaks of interest. This will depend on the precision that is required in the final results. However, where there is any doubt about precision, the analysis shall be repeated so that repeatability of the result can be verified.

6.8 All the relevant measurement parameters (take-off angle, specimen tilt, accelerating voltage, etc.) shall be recorded.

NOTE In EDS, since the spectrometer resolution is of the order of 100 eV, the complex series of characteristic X-ray line emissions appear as a few broad peaks in the digitised energy spectrum. Electronic counting losses are usually corrected automatically by slowing down the system clock and the spectrum is recorded for a preset "live time" in seconds, where "live" seconds are slightly longer than real seconds. The area of a peak, in counts divided by the preset live time, gives the intensity of X-rays striking the active area of the detector. On the assumption that the same incident electron beam current and same recording live time are used, the peak area in counts is an appropriate measure to compare X-ray intensities for quantitative analysis, and therefore the terms "peak intensity" and "peak area" are used in this International Standard.

7 Data reduction

7.1 General

Information contained in the spectra from the specimen consists of peaks arising from the characteristic X-rays of the elements present in the analysed volume of the specimen. Although the intensity of a peak is related to the amount of the element present in the specimen, the relative intensity of the peaks from various elements shall not be taken to represent the relative concentrations of the elements.

7.2 Identification of peaks

The identity of all peaks in the spectrum shall be determined, taking care to allow for the possibility of peak overlap, see Annex B (see References [9] and [10] in the Bibliography).

Automatic peak identification software may be provided by the manufacturer of the equipment and some software will deal with overlapping peaks. However, performance depends on the accuracy of modelling of peak profile and, consequently, different combinations of software, electronics and detectors can produce different results for the same specimen.

Alternatively, manual identification of peaks should be performed in a systematic manner beginning with the most intense peaks, see Annex A. The operator shall confirm the identification of all elements by reference to published peak intensity data, with particular reference to the energies and relative intensities of the lines within each of the observed K, L or M series. Incorrect peak intensity ratios or irregularly shaped peaks may indicate the presence of an interfering element and should be investigated whilst making allowance for the loss of intensity which can occur for low energy lines near the lower limit of detector response, or when the overvoltage is inadequate for the line in question. All the observed peaks in the spectrum shall be accounted for, including the possible appearance of escape peaks or sum peaks that occur when high count rates are used.

Suitable peaks, from which to analyse for the concentration of each element present, shall then be selected. For example, for an accelerating voltage of 20 kV, the following lines are suitable for quantification: Z = 11-30 K lines, Z = 29-71 L lines, Z = 72-92 M lines.

7.3 Estimation of peak intensity

In order to calculate the net peak intensity of interest, it is necessary to subtract the underlying background (normally done by the software). This can be removed by modelling and subtraction from the whole spectrum, by digital filtering, or, by linear interpolation between points on either side of the peak. Background subtraction is less likely to be accurate if estimated over a large energy range. The choice of method will be largely dependent on the facilities available within the analysis software, and their accuracy in relation to the intended overall accuracy of the analysis.

In the event of overlapping peaks, deconvolution routines may be available with the software, or manual estimates, made using the relative peak intensities of the various peaks that appear in the spectrum of a pure element, offer ways of correcting for this. Whatever approach is used, validation shall be undertaken using CRMs/RMs as specimens (see Reference [12] in the Bibliography).

7.4 Calculation of k-ratios

The extracted peak intensities (after background subtraction) for the elements found in the specimen, divided by the intensities of the corresponding peaks in the spectra of the pure elemental references, will give the k-ratios. When pure elements are not available and compound reference materials are employed, the observed reference peaks shall be corrected for matrix effects; such corrections are included in most software packages.

As an alternative to the use of reference materials, the k-ratios may be obtained by comparing specimen peak intensities to elemental intensities held in, or calculated by, one of the many “standardless” procedures that are available (see 7.7).

7.5 Matrix effects

The set of k-ratios for the elements identified in the specimen are corrected for matrix effects by applying one of many available correction routines. The corrections allow for atomic number (Z), X-ray absorption (A), and fluorescence (F) effects leading to the frequently used generic title of ZAF. Various other procedures have been evolved to optimise performance and may be preferred to the purely numerical ZAF routines. For example, the “phi-rho-Z” model also allows the depth distribution of the generated X-rays to be displayed. This is of particular value when assessing whether the analysis has been confined to the desired depth (or area) within the specimen.

Attention shall be paid to the analytical totals after this correction, but before any normalisation is considered. When using a procedure where a separate measurement is made on at least one reference material, un-normalised analytical totals in the range 95 % to 105 % are considered acceptable. Values outside this range shall be investigated to determine whether unidentified elements are present, including those of atomic number 10 and below, or whether instrumental instabilities have occurred during the analysis.

Where the analysis total is < 100 % and a single element with $Z < 11$ is also known to be present, its concentration can be inferred by difference, providing the effects of this element on the matrix corrections is known. This is particularly true if the element is oxygen and it is combined in a stoichiometric manner. Measurement of an element by difference can lead to large relative errors in the element's concentration, particularly when concentrations are low.

7.6 Use of reference materials

For quantitative analysis by X-ray microanalysis, the reference materials should be certified wherever possible. However, reference materials with a composition close to those of the specimens can be used in two ways:

a) a specimen from such a material can be included in every batch of analyses to verify that satisfactory results are being obtained, and to provide information on the uncertainty associated with the analysis;

b) it may be acceptable to make a direct comparison between the peak intensities observed in the specimen and in the reference material in order to obtain an estimate of the specimen composition. This may be the optimum approach if suitable elemental reference materials are not available.

The operating conditions under which the specimen and reference material data are obtained shall be the same.

NOTE Modern software can often compensate for any differences in operating conditions. Multi-element reference materials are available which provide for a daily monitoring of calibration, i.e. checks on relative peak intensities and peak positions.

7.7 Standardless analysis

The standardless analysis routines mentioned in 7.4 can be employed when elemental reference materials are not available at the time the analysis is undertaken. These routines provide estimates of elemental concentration which are considerably more accurate than those derived from uncorrected relative peaks. The standardless routines provide correction for specified excitation conditions and geometries. The k-ratios in these procedures are obtained by reference to elemental peak intensities derived by calculation, or extracted from a library of elemental or compound spectra (or profiles) provided by the manufacturer and augmented, or replaced, by spectra obtained by the user on previous occasions. A total relative uncertainty better than $\pm$ 10 % relative may be achieved. However, greater errors can be expected when the analytical conditions used are different from those specified for the standardless procedures and where low concentrations exist.

In its simplest form, the standardless analysis provides estimates of the relative elemental concentrations and forces the sum to be 100 %, yielding a plausible result even if elements are omitted from the analysis, the wrong elements are specified, or there are large errors in the determination of peak intensities. If some elements cannot be analysed because there is no suitable peak available, then this shall be noted on the printout of results, because the relative concentrations calculated by standardless analysis will not include the effect of these missing elements on the X-ray intensity corrections for other elements (see Reference [1] in the Bibliography).

A more reliable procedure may include measurement on one or more reference materials to enable estimates of absolute concentrations to be obtained. Unnormalised totals may then be used as a tool to diagnose the possibility of the presence of undetected elements in the specimen.

Validation is an essential part in the derivation of the uncertainty associated with the standardless approach and shall be performed on known materials with similar characteristics to those of the specimens to be analysed; particular attention should be paid to matching the experimental conditions to those required by the standardless procedure (see ISO/IEC 17025, 2005, Subclauses 5.4.5 and 5.9).

Validation of the method (software and procedure), shall be performed prior to any analyses being done. This can be accomplished using certified reference materials.

7.8 Uncertainty of results

7.8.1 General

Subclauses 7.8.2 and 7.8.3 offer guidance for uncertainty estimation where in-house development and validation is performed (see References [13] to [16] in the Bibliography).

7.8.2 Routine analyses on repeated or similar specimens

The analyst shall establish the in-house reproducibility and accuracy of measurement for typical specimens analysed in the laboratory, and should also validate the method to ensure that it is fit for the purpose.

The reproducibility of a measurement shall be established from repeat testing of the same specimen under nominally the same conditions at intervals of time which are long compared with the time of analysis. This can incorporate different operators and different analysis points within the same phase. This component of uncertainty will include a number of the factors listed in Annex C.

Participation in proficiency testing schemes, round robin specimen analyses will provide a useful measure of the reproducibility among laboratories and may introduce evidence of other uncertainties in the analyses from an individual laboratory.

NOTE The repeatability of a measurement is obtained from repeat readings obtained by the same operator using the same instrument operating under the same conditions and examining the same area of specimen during a relatively short time period. This component of uncertainty will usually include fewer of the factors listed in Annex C.

The measures of repeatability/reproducibility provide some measure of the combined uncertainty from random sources.

A measure of the accuracy of the result will be obtained if these repeat analyses are done on a certified reference material (CRM) using identical operating conditions. This approach will also establish the traceability of the results to recognised reference materials, and identify the occurrence of systematic errors. The alternative is for the laboratory to establish the accuracy using results obtained by an established analytical method or methods.

The contributions from other factors can be estimated using professional judgement or the methods prescribed in the Eurachem document [13].

Combining the measures of reproducibility and accuracy will provide a measure of the uncertainty.

Factors that contribute to the uncertainty of measurement shall be identified and their effects minimised. Typical factors are associated with the instrument (hardware and software), changes in ambient conditions, the analytical procedure, the specimen and the operator. Large differences in the chemical composition of the specimen over small areas (heterogeneity) can be a major source of uncertainty in the measurement. Examples of such factors are listed in Annex C.

7.8.3 Non-routine analyses

Non-routine analyses carried out using a full suite of elemental/compound RMs, and following well-established procedures, can be expected to be associated with uncertainties of the same order as those established in 7.8.2 for similar elements in similar matrices. The operator shall take great care to ensure that problems such as those given as examples in Annex C have not occurred, and shall in any event indicate that any uncertainties quoted are typical.

Analyses carried out using experimental parameters (line energies, operating voltages, surface condition, unusual matrix material, etc.) outside the normal envelope within which uncertainties have been determined as in 7.8.2, or carried out using “standardless” procedures, may need to be reported with uncertainties many times larger than the norm. Annex C includes examples of parameters which need to be considered when attempting to attribute uncertainty values to specific analyses, and should assist the analyst in establishing appropriate caveats to be attached to the results.

Typical data collected over several years by one laboratory, and an interlaboratory comparison, is shown in Annex E.

7.9 Reporting of results

The reporting of the results shall conform with ISO 17025 and specify:

a) the name and address of the laboratory;

b) the name and address of the client;

c) a unique identifier of the certificate;

d) some unique form of sheet identifier (p. ... of ...);

e) date of test and issue of report;

f) date of receipt of specimen;

g) specimen details;

h) details of the calibration procedure;

i) details of the test procedure (instrument details, operating conditions, software used, validation);

j) the results and a measure of their uncertainty;

Analysis results that have been normalised to 100 % should be accompanied by a clear disclaimer, to say that the composition is approximate and the total is not to be used as a statement of validity. This should be reflected in the value of the uncertainty quoted.

k) signature of the person taking responsibility.

Annex A
(informative)

The assignment of spectral peaks to their elements

A.1 The procedure described in A.2 to A.10 should be performed.

A.2 Prior to the analysis, wherever possible, request bulk chemistry of the specimen and the identity of all elements.

A.3 Ensure that all checks relating to preliminary precautions (Clause 5) are completed. Collect a spectrum from the specimen, choosing an accelerating voltage of typically between 10 kV and 20 kV with a beam current giving, wherever possible, a total count rate of at least 2 000 counts/s to 3 000 counts/s and a corresponding dead time of 20 % to 30 %. Collect about 50 000 counts for the largest peak, or 250 000 counts in the total spectrum. This normally corresponds to approximately 100 s live time.

NOTE The above count rate corresponds to a typical Si-Li detector. Some commercial detectors allow faster count rates at the specified dead times. There is normally a reduction in the resolution of the peaks at these higher count rates.

A.4 Identify peaks which are statistically significant, i.e. with an intensity of $> N(b) + 3[N(b)]^{1/2}$, where N(b) is the mean value of the background intensity.

Should a weak peak corresponding to an element that is of particular interest be apparent, the spectrum should, the specimen providing, be collected for a longer period to check if the peak is significant. Possible specimen drift shall be checked if the dimensions of the analysis volume approach those of the feature of interest. Also, the elements present can be checked by WDS if the system is available. The limits of detection for WDS are generally 0,01 % (mass fraction) and, under favourable condition, 0,001 % (mass fraction) (10 parts per million).

A.5 Locate the peak with the greatest intensity.

A.6 Relate the measured X-ray energy at the peak position to the element using

a) an X-ray energy slide rule,

b) a graph of atomic number versus energy, or

c) one of the tabulations or the “KLM” markers provided by the software package (see References [10] and [11] in the Bibliography).

NOTE Tabulations although comprehensive are slow to use; the slide rule and “KLM” markers may not have all the relevant peaks included.

A.7 Having assigned the largest peak, confirm the presence and then assign:

a) the lower intensity (K,L,M…) peaks from the same element;

NOTE 1 At low energies below 3 keV, the subsidiary lines are not fully resolved.

b) the sum peaks;

NOTE 2 The intensity of these peaks increases with increasing count rate.

c) the escape peaks;

NOTE 3 The magnitude of the escape peaks are a constant fraction of that of the parent peak, ranging from 1 % for P Kα to 0,01 % for Zn Kα. This magnitude is higher for Ge detectors. ranging from 17 % for Se Kα down to 7 % for Ru Kα.

A.8 The next highest intensity peak remaining shall be assigned and the process repeated from step A.5 to step A.7, until all the peaks are assigned to an element, sum peak or escape peak.

NOTE As the absolute intensity of the peaks decreases, it becomes increasingly difficult to detect the smaller intensity members of the family of peaks. Thus, the confidence of assigning elements at minor and trace levels becomes less than for the major elements.

Below 1 keV, the lower energy peaks from heavier elements (L peaks) can interfere with the Kα peaks of the light elements and this can make the unambiguous identification of light elements very difficult. Peak deconvolution at these low energies shall be performed carefully, since poor counting statistics are associated with the light elements. WDS with the higher spectral resolution should be considered.

A.9 The interference of coincident energies of peaks from different elements shall be checked, see Annex B.

A.10 The result shall be a spectrum with every peak assigned to an element or its associated escape peak and sum peaks. Any interferences shall be clearly marked.

Annex B
(informative)

Peak identity/interferences

Ambiguities arise in the identification of a peak in the spectrum when characteristic peaks from two or more elements are sufficiently close to be indistinguishable from each other, and the operator should be aware of this possibility. The magnitude of the energy separation between two peaks below which this problem can occur is dependent on the detector resolution and the accuracy of the calibration, but typically a value of 30 eV can be critical; peaks separated by more than this figure should not be confused by either automatic or manual identification procedures.

A first step in an identification process is likely to be a search for a match between the energy of a strong peak in the spectrum and the energy of a primary line from one of the elements. Primary lines, i.e. Kα, Lα, or Mα are considered first, as they are normally the most intense within a given K, L, or M series, and for a 30 eV criterion the following ambiguities can occur:

C-K or Ca-L

N–K or Sc–L or Ti-L

O-K or V–L or Cr-L

F-K or Mn-L or Fe-L

Na-K or Zn-L

Mg-K or As-L

Al-K or Br-L

Rb-L or Ta-M

Si-K or Ta-M

Y-L or Os-M

P-K or Zr-L or Pt-M

Au-M or Nb-L

Nb-L or Hg-M

Mo-L or Tl-M

S-K or Mo-L or Pb-M

Tc-L or Bi-M

Ar-K or Ag-L

Ag-L or Th-M

K-K or In-L

Sc-K or Xe-L

Ti-K or Ba-L

Zn-K or Re –L

As-K or Pb-L

This list does not include the rare earths, nor does it consider ambiguities between primary lines of one element and secondary lines (e.g. Kβ, Lβ, Lγ, etc.) of another.

Annex C
(informative)

Factors affecting the uncertainty of a result

C.1 Factors

The uncertainty of analytical results can be affected by the following factors:

Specimen heterogeneity
Specimen roughness – uncertain geometry, shadowing
Polishing artefacts – contamination, chemical effects
Conductive coating – not the same for specimen and CRM/RM, contribution of the coating to the analysis
Specimen charging – poor grounding, current/voltage too high
Incorrect geometry – working distance, tilt, elevation and azimuth angles of detector mounting to specimen chamber
SEM/EPMA instability – kV, beam current, spot position
Detector degradation – stability, resolution, calibration, contamination
Process time – long enough for resolution, short enough for acceptable dead time
Unsuitable beam settings – kV (excitation, resolution, charging), current (statistics, probe size)
Pulse processor setting errors - not same specimen/reference material
Inadequate statistics – beam current/count time combination
Element misidentification – overlaps, escape peaks, pile-up peaks – software efficiency
Background subtraction errors – modelling, interpolation, filter performance
CRM/RM errors – preparation, positioning, coating
Stored/calculated profile errors – overlapping lines, incorrect conditions
Matrix correction errors – no accepted tabulations
Beam spill – beam size>feature size, fluorescence effects across boundaries
Missing elements - matrix correction errors, low analytical totals, normalisation errors

C.2 Method

An approach to a measure of the uncertainty is the following.

a) Specify what is being measured, including its relationship with the input quantities.

b) Identify uncertainty sources (see C.1 to collect a structured list),

   — identify the effects on a result (cause and effect diagram or “fishbone” diagram), and

   — simplify and resolve duplication.

c) Quantify uncertainty (measure or estimate).

d) Calculate combined uncertainty.

C.3 Measurements

a) Precision data can be obtained from measurements collected over an extended time to allow for natural variation of all factors affecting the result. The options for this are the following.

   1) Analyses of a typical specimen performed at different times.

   2) Replicate analyses of several specimens performed at different times.

   3) Multifactor experimental designs, analysed by ANOVA (analysis of variance between groups) to provide separate variance for each factor.

NOTE Precision can vary with concentrations (see Annex E).

b) Accuracy (freedom from bias) data can be obtained from:

   1) Repeated analysis of relevant CRM.

   2) When reference material is only approximately representative, additional factors should be considered, such as differences in homogeneity and composition.

   3) Comparison of results with those of a reference method.

c) Those relating to any additional factors which contribute to the total uncertainty.

Annex D
(informative)

Analysis of elements with atomic number < 11

D.1 The quantitative analysis of the lighter elements and also heavier elements, if L- or M-lines are used, introduces a number of problems in addition to those documented in the body of this International Standard. These primarily arise because the specimens give spectra exhibiting overlap of peaks corresponding to L and M lines with those from low energy K lines. The operator is advised to proceed with great caution and be aware of the following points. Even qualitative analysis will be inaccurate, unless the sources of all spurious contributions to C and O in particular have been eradicated.

Validation of the experimental technique using reference materials should be an essential feature of such work.

D.2 With EDS, peaks at low energies are much closer together and their separation is not as good as that found at higher energies. Peak overlap will be more frequent, with the K peaks of the lighter elements overlapping with the L and M peaks of heavier elements. The profile of the L and M peaks below 1 keV is not accurately known, and the determination of peak intensities when any overlap (e.g. Ti/N , V/Cr/O, Mn//Fe/F) occurs is dependent on the method of deconvolution of the peaks implemented in the software.

D.3 The occurrence of peak overlap also introduces difficulties in background correction. An extrapolated background curve will be inaccurate if the detector efficiency is not accurately known, or has changed, because of contamination build-up, since the system was installed.

D.4 With an accelerating voltage of 20 kV, the strong absorption of low energy X-rays, together with the large uncertainty in their absorption coefficients, gives rise to uncertainties in peak intensity far greater than those for high energy peaks. With a low accelerating voltage, absorption may be less, but the effect of the conductive film or contamination film becomes a problem, as does the reduced overvoltage on the higher energy peaks. At 20 kV, a surface tilt of a few degrees can change some low energy peak intensities by 10 % or more. Furthermore, at low kV, the presence of the thin surface-oxide layer, commonly found on most specimens, is accentuated so the oxygen weight percent recorded is not representative of the underlying bulk composition.

D.5 With a conductive coating of carbon, about 10 % of the nitrogen Kα signal is absorbed by a carbon film of 20 nm thickness. The film itself also contributes to the measured carbon peak intensity.

D.6 A specimen chamber free of contamination is desirable for quantitative analysis of light elements. Carbon contamination can build-up on the specimen surface under the beam, during analysis. This problem can be negligible in a very clean vacuum system, but build-up of a thickness of several nanometres per minute is possible. As with a conductive film, a carbon contamination layer absorbs low energy X-rays and contributes to the carbon signal. Oil may condense on the detector window and cause a gradual reduction in low energy efficiency. Water vapour may permeate a thin polymer window, and some materials within the detector vacuum may outgas over a long period and cause icing and contamination to build up on the front surface of the detecting crystal. Low energy lines are more likely to be affected by all such causes of variable detector efficiency.

D.7 Spurious carbon X-rays can also be generated by backscattered electrons hitting specimen surfaces, which are earthed using a carbon paint. Surfaces that have been coated with carbon within the chamber or in the magnetic electron trap in front of the detector may also contribute to the carbon signal.

D.8 At count rates in excess of a few kilocounts/s, a carbon sum peak can be mistaken for the oxygen Kα peak.

Annex E
(informative)

Example data from a reproducibility study within a laboratory and between laboratories

Table E.1 shows EDS results obtained in a single laboratory from a CRM, NBS S479a (see Reference [17] in the Bibliography). Twenty readings were obtained on 18 occasions over a period of 8 years. Two operators were involved. All results were ZAF corrected (see 7.5) and then normalised to 100 % to allow for other minor elements present. All analyses gave totals $>$ 97 % prior to normalisation. A significant difference, particularly for Cr, between the bulk chemical analysis and that obtained by microanalysis methods can be observed. Systems in which a strong fluorescence exists are liable to give larger inaccuracies for the fluoresced element. The fluorescence correction theory also requires specimen homogeneity over a distance of several ($\sim$ 50) micrometres from the beam and that is unrealistic for some specimens.

Table E.1 — Range, average and standard deviation (SD) for the microanalysis of the CRM NBS S479a

	Range % (mass fraction)	**Average** % (mass fraction)	**1(SD)**	**Chemical analysis** % (mass fraction)
Fe	70,5 to 69,6	70,3	0,27	71,0
Cr	19,7 to 18,9	19,3	0,27	18,1
Ni	10,3 to 10,6	10,5	0,10	10,9

Table E.2 shows the results of EDS analyses on the same sample in six different laboratories, together with WDS and chemical analyses performed at NIST. The results in this table were obtained having first calibrated the systems with pure elemental materials and also having calibrated the spectrometers. The WDS examination confirmed that the sample was not homogeneous and that the Cr and Ni mass fraction could vary by $\pm$ 0,5 % . Also, while the mass fraction of Cr from EDS and WDS was significantly different from the wet chemical data, even at the certifying laboratory, all the EDS and WDS results agreed within their 95 % uncertainty limits. This would suggest that, for analysis of certain materials, while methods may show differences, those coming from techniques analysing micrometre-sized volumes are remarkably consistent. This, in turn, reflects a consistency in the software and hardware of the systems used and also for the methodology and calibration procedures in the individual laboratories. It also highlights the need to choose reference materials with care and validate analytical methods.

Table E.2 — Interlaboratory comparison of the elemental composition [% (mass fraction)] and standard deviation for microanalysis of CRM NBS S479a

Laboratory	Fe % (mass fraction)	2(SD)	Cr % (mass fraction)	2(SD)	Ni % (mass fraction)	2(SD)	Number of analyses
A	70,9	—	18,8	—	10,3	—	2
B	71,0	0,21	19,2	0,15	9,8	0,12	10
C	70,5	0,13	19,2	0,09	10,2	0,07	5
D1	70,5	0,4	18,9	0,19	10,6	0,20	20
D2	70,3	0,18	19,3	0,14	10,4	0,13	20
E (WDS)	70,5	0,21	19,2	0,13	10,3	0,18	40
F	69,5	1,5	19,8	0,2	10,7	0,4	5
NIST (WDS)	70,7	0,57	19,45	0,28	10,65	0,25	
NIST (Chemical)	71,0		18,1		10,7		

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